

**REMARKS**

The reopening of prosecution as set forth in Item 1 on page 2 of the Office Action mailed January 23, 2009, is noted. In view thereof, Applicants exercise the option (1) set forth, and file the present reply under 37 C.F.R. §1.111, so as to proceed with prosecution of the above-identified application and to avoid abandonment thereof.

That is, Applicants have amended their claims in order to further clarify the definition of various aspects of the present invention. Specifically, Applicants have amended claim 1 to recite that a plasma is generated from the hydrobromic gas and chlorine gas while supplying Si atoms to the plasma, the Si atoms being supplied to the plasma by applying the high-frequency power to the Si wafer; and to recite that the aluminum fluoride deposit adhered to the interior of the processing chamber is removed "by reaction between the aluminum fluoride deposit and the plasma containing Si atoms. Claim 3 has been amended to recite that the plasma additionally contains Si atoms; and in light of amendments to claim 3, claim 15 has been cancelled without prejudice or disclaimer. Claims 10 and 13 also have been cancelled without prejudice or disclaimer, whereby remaining issues are simplified. Claims 8 and 9 have been amended to recite that the application of high-frequency power to the Si wafer through the substrate holder supplies the Si atoms to the plasma. And claims 16 and 17 respectively have been amended to recite that a portion of the material constituting the vacuum container includes Si, from which Si atoms are supplied to the plasma, and that cleaning the aluminum fluoride deposit in the vacuum container is performed using the plasma containing the chlorine gas and the hydrobromic gas and additionally the Si atoms; and to recite that the plasma

containing chlorine gas and hydrobromic gas additionally contains  $\text{SiCl}_4$  gas “so as to provide Si atoms contained in the plasma”.

Note, for example, pages 31-33 of Applicants’ specification; see also the reaction procedure as described, for example, on pages 13 and 14 of Applicants’ specification. See especially equation (6) on page 14 of Applicants’ specification, showing the reaction with silicon atom.

Applicants respectfully submit that all of the claims presented for consideration by the Examiner patentably distinguish over the teachings of the references applied by the Examiner in rejecting claims in the Office Action mailed January 23, 2009, that is, the teachings of the U.S. patents to Kitsunai, et al., No. 6,186,153, to Qian, et al., No. 6,136,211, and to Benzing, No. 4,786,352, under the provisions of 35 U.S.C. §102 and 35 U.S.C. §103.

It is respectfully submitted that the teachings of these references as applied by the Examiner would have neither taught nor would have suggested such a method for cleaning a plasma processing apparatus as in the present claims, including, inter alia, introducing a mixed gas of hydrobromic and chlorine gas into a processing chamber, and generating a plasma from the hydrobromic gas and chlorine gas while supplying Si atoms to the plasma, the Si atoms being supplied to the plasma by applying high-frequency power to the Si wafer; and removing an aluminum fluoride deposit adhered to the interior of the processing chamber by reaction between the aluminum fluoride deposit and the plasma containing Si atoms. See claim 1.

In addition, it is respectfully submitted that the applied references would have neither disclosed nor would have suggested such a method for cleaning a plasma

processing apparatus as in the present claims, including, inter alia, providing a period for cleaning an aluminum fluoride deposit in the vacuum container by generating plasma containing chlorine gas and hydrobromic gas and, additionally, Si atoms to create a gas-phase reaction product either each time after plasma processing a wafer or plural wafers or before and after plasma processing. See claim 3.

Furthermore, it is respectfully submitted that the teachings of the applied references would have neither disclosed nor would have suggested such method for cleaning as in the present claims, having features as in claims 1 and 3 as discussed previously, and, additionally, wherein the process further includes placing a Si wafer, with no patterns printed thereon, on the substrate holder when the plasma including chlorine gas and hydrobromic gas is discharged, with high-frequency power being applied to the Si wafer to supply Si atoms to the plasma (see claims 8 and 9), in particular, wherein the high-frequency power corresponds to a frequency of 400 kHz and is equal to or greater than 0.11 W per unit area of the wafer (see claim 9); and/or wherein a portion of material constituting the vacuum container includes Si, from which Si atoms are supplied to the plasma as in claim 16, with the cleaning performed using the plasma containing the hydrobromic and chlorine gases and additionally the Si atoms; and/or wherein the plasma containing chlorine and hydrobromic gasses additionally contains  $\text{SiCl}_4$  gas so as to provide Si atoms contained in the plasma (see claim 17).

Moreover, it is respectfully submitted that the teachings of the applied references would have neither disclosed nor would have suggested such cleaning method as in the present claims, having features as discussed previously in

connection with claim 3, and further including a period for generating plasma containing SF<sub>6</sub> prior to the period for generating plasma with the chlorine and hydrobromic gasses. See claim 14.

Furthermore, it is respectfully submitted that even assuming, arguendo, that the teachings of references as applied by the Examiner would have established a prima facie case of obviousness, the evidence of record in the above-identified application, namely, the experimental data in Applicants' specification, overcomes any such prima facie case of obviousness, establishing unobviousness of the presently claimed subject matter. In this regard, attention is particularly directed to Embodiment 4 on pages 22-27 of Applicants' specification, and the results shown in Table 1 on page 23 thereof. As described in the paragraph bridging pages 23 and 24 of Applicants' specification, from Table 1, it can be seen that aluminum fluoride cannot be cleaned by SF<sub>6</sub>. Moreover, use of an SiO<sub>2</sub> wafer cannot achieve cleaning of aluminum fluoride using Cl<sub>2</sub>. By supplying Si atoms to the plasma, e.g., by placing an Si wafer and by applying 20W of bias power, cleaning is performed. Note also the sole two full paragraphs on page 24 of Applicants' specification.

This evidence, in Applicants' specification, of unexpectedly better results achieved according to the present invention must be considered in determining the question of obviousness under 35 U.S.C. §103. In re DeBlauwe, 222 USPQ 191 (CAFC 1994). Properly considered, this evidence establishes unobviousness.

The present invention relates to a method for cleaning a plasma processing apparatus, particularly useful in connection with cleaning a vacuum chamber having an aluminum fluoride deposit therein. Such deposit can cause problems if not cleaned, in that such deposit builds up and can affect the plasma, and can also flake

off and deposit on the substrate being processed, causing defective products and thus undesirably reducing yield.

It has been known that when a gas containing fluorine is used during plasma processing, aluminum fluoride is generated, which is a stable compound having low vapor pressure and which cannot be removed easily. Various methods for removing aluminum fluoride have been proposed. One method uses  $\text{Cl}_2$  gas to decompose  $\text{AlF}_3$  into  $\text{AlCl}_3$ , and another method proposed decomposing and removing  $\text{AlF}_3$  using  $\text{H}_2\text{O}$  and  $\text{Cl}_2$ . As for these previously proposed cleaning methods, note the paragraph bridging pages 5 and 6 of Applicants' specification.

However, recently materials of the wafers, and gasses used in the plasma processing, have diversified, and the problem of deposits that cannot be removed by conventional plasma cleaning methods has become more significant. Note the last full paragraph on page 6 of Applicants' specification. Therefore, a more effective method for cleaning the reaction chamber is required, for enhancing throughput.

Against this background, Applicants provide a method wherein contaminants, such as deposits, in particular, deposits of aluminum fluoride, in the vacuum processing chamber, can be safely and effectively removed, in a short time, thereby avoiding reductions in throughput. Applicants have found that by forming a plasma including a mixed gas of hydrobromic gas and chlorine gas, and also containing silicon atoms, in apparatus in which a silicon wafer is placed on an electrode for holding the object to be processed, and with a high frequency power applied to the Si wafer so as to provide the silicon atoms in the plasma; and/or wherein the plasma generated additionally includes silicon atoms, which reacts with fluorine to create a gas-phase reaction product, such plasma containing Si atoms can be used to

remove aluminum fluoride deposits adhered to the interior of the processing chamber, effectively and in a short time. Note especially Embodiment 1 on pages 9-14 of Applicants' specification, further evidence of unexpectedly better results achieved by the present invention.

In particular, Applicants have found that by including Si atoms in the plasma containing chlorine gas and hydrobromic gas, a further improvement of speed in removing aluminum fluoride is achieved. Note Embodiment 4 on pages 22-27 of Applicants' specification. Note especially Table 1 on page 23, and the discussion in connection therewith in the paragraph bridging pages 23 and 24, of Applicants' specification; see also Embodiment 2 on pages 16 and 17.

In addition, Applicants have found that with various processing, carbon deposits may occur in the processing chamber; and that such carbon deposits can be removed effectively and efficiently, by generating plasma containing SF<sub>6</sub> prior to generating the plasma containing the chlorine and hydrobromic gasses, and additionally Si atoms. See, e.g., the first full paragraph on page 27 of Applicants' specification.

Qian, et al. discloses a method of etching a substrate in an etching chamber, that reduces or entirely eliminates etch residues on the chamber surfaces and provides highly consistent and reproducible etching performance. In the described method, the substrate is etched and, simultaneously, the etching chamber is cleaned of etch residue. A substrate is placed in the chamber, and a plasma is formed from process gas introduced into the chamber to simultaneously etch the substrate and clean etched residue deposited on the chamber surfaces. The process gas comprises (i) etching gas for etching the substrate, thereby forming etch residue on

chamber surfaces, and (ii) cleaning gas for cleaning the etch residue formed on the chamber surfaces, the volumetric flow ratio of cleaning gas to etching gas being selected so that the etch residue is substantially entirely moved from the chamber surfaces upon completion of the etch process. Note, column 3, lines 44-60. Note also column 8, lines 50-58, describing the etchant gas for etching the substrate. See also column 11, lines 21-46, disclosing a cleaning gas added to the etchant gas, the cleaning gas comprising CF<sub>4</sub> at a full rate of 80 sccm, to provide a volumetric ratio of cleaning gas to first etchant gas of about 2:3. See also column 13, lines 13-17.

The Examiner has pointed to column 9, lines 6-17 of Qian, et al. This portion of the reference discloses simultaneous etching of one or more layers of a substrate and cleaning of the plasma processing chamber, utilizing, as the etchant gas, one or more of Cl<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, HBr or He-O<sub>2</sub>, and a cleaning gas comprising one or more of NF<sub>3</sub>, CF<sub>4</sub> or SF<sub>6</sub>.

It is emphasized that even as applied by the Examiner, Qian, et al. discloses an etchant gas containing at least one of Cl<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, HBr or He-O<sub>2</sub>, with a different cleaning gas. Moreover, this reference does not disclose, nor would have suggested, adding Si atoms to the plasma. It is respectfully submitted that this reference does not disclose, nor would have suggested, such cleaning as in the present claims, utilizing as a cleaning gas the mixed gas of hydrobromic gas and chlorine gas, by generating plasma containing chlorine gas and hydrobromic gas and additionally Si atoms, as in claim 3; and/or such method as in claim 1, including generating a plasma from the hydrobromic gas and chlorine gas while supplying Si atoms to the plasma, particularly wherein the Si atoms are supplied to the plasma by applying high-frequency power to the Si wafer (note, in particular, claims 1, 8 and 9).

It is respectfully submitted that Qian, et al., would have taught away from such cleaning procedure as in the present claims, including generating a plasma from the hydrobromic gas and chlorine gas while supplying Si atoms to the plasma, or wherein the plasma contains Si atoms in addition to the chlorine and hydrobromic gases, as Qian, et al. specifically discloses a cleaning gas including different gases from chlorine and hydrobromic gases when the etchant gas comprises at least one of Cl<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, HBr or He-O<sub>2</sub>.

The contention by the Examiner in the paragraph bridging pages 3 and 4 of the Office Action mailed January 23, 2009, that Qian, et al. discloses providing a period for cleaning a residue deposited in the etching chamber by generating a plasma from a processing gas including Cl<sub>2</sub>, HBr, N<sub>2</sub> and additional element, is respectfully traversed. It is respectfully submitted that the cleaning gas in Qian, et al. comprises one or more of NF<sub>3</sub>, CF<sub>4</sub> or SF<sub>6</sub>. Note the comparison of cleaning when using SF<sub>6</sub> as the plasma gas species, in Table 1 on page 23 of Applicants' specification. Such disclosure in Qian, et al. would have taught away from the presently claimed process, utilizing the mixture of gases for the plasma as recited in the present claims, and wherein the plasma additionally includes Si atoms.

The additional contention by the Examiner in the first full paragraph on page 4 of the Office Action mailed January 23, 2009, that Qian, et al. discloses steps for removing residue from the etching chamber wall that "are similar to those instantly claimed" is respectfully traversed. The cleaning gas in Qian, et al., even from the disclosure of this reference applied by the Examiner, is different from the mixture of gases from which the plasma is generated, in the present claims; and, clearly, Qian, et al., would have neither disclosed nor would have suggested supplying Si atoms to



the plasma while generating the plasma (or wherein the plasma generated additionally includes Si atoms). Clearly, the steps in Qian, et al., are not similar to those of the present claims, and the process in Qian, et al. would have neither disclosed nor would have suggested the presently claimed process, and advantages achieved thereby.

The contention by the Examiner in connection with claim 16, in the second full paragraph on page 6 of the Office Action mailed January 23, 2009, is respectfully traversed. It is respectfully submitted that the Si contained in the vacuum container is used in the presently claimed process. That is, as described in Applicants' specification, for example, in the first full paragraph on page 33 of Applicants' specification, and as in the present claims, Si atoms are supplied to the plasma from the portion of material constituting the vacuum container that includes Si. Note, particularly, claim 16 as presently amended, reciting that the portion of material constituting the vacuum container includes Si, "from which Si atoms are supplied to the plasma". While reciting a component of the vacuum container, as this component participates in the method, it must be considered in determining patentability of the method.

Kitsunai discloses a method for dry cleaning the interior of a semiconductor manufacturing apparatus, which includes the steps of removing etching reaction products, and removing either ion sputtered constituents of those materials of the internal structure members of the manufacturing apparatus or chemical compounds of such apparatus materials and the etching gas being used, by a dry cleaning process which makes use of a chosen gas that contains therein a material having an interatomic bonding energy, with respect to elements constituting a gas for use

during an etching and a cleaning step, which is greater in value than the atomic bonding energy between elements constituting a material to be etched and elements constituting a gas or gasses used during the etching and cleaning processes. See column 2, lines 48-63, see also column 4, lines 30-37 and 45-47. Note also column 5, lines 36-42. Note, in addition, column 8, lines 20-32, disclosing cleaning of aluminum fluoride, using as the cleaning gas a mixture of  $\text{Cl}_2$  and  $\text{BCl}_3$  added thereto.

Clearly, and as acknowledged by the Examiner in the third paragraph on page 7 of the Office Action mailed January 23, 2009, Kitsunai, et al., would have neither disclosed nor would have suggested generating a plasma containing chlorine gas and hydrobromic gas; moreover, this reference would have neither disclosed nor would have suggested generating a plasma containing such mixed gases and additionally Si atoms, and advantages achieved thereby as discussed in the foregoing.

It is respectfully submitted that the additional teachings of Benzing would not have rectified the deficiencies of Kitsunai, et al., such that the presently claimed invention as a whole would have been obvious to one of ordinary skill in the art.

Benzing discloses cleaning devices for removing deposits and/or contamination from processing chamber walls, using a plasma formed within the processing chamber to achieve such cleaning. The device and method disclosed in this patent consists of two or more electrodes that may be shaped as interleaving fingers and that are fixtured on the exterior of a process chamber that is constructed primarily of dielectric material. This patent goes onto to describe that by evacuating the chamber, admitting a cleaning gas and applying RF potential, a plasma is formed

within the chamber; and by appropriate choice of the cleaning gas and configuration of the electrodes, either the interior walls of the chamber together with any tooling can be cleaned, or the surfaces of a substrate placed within the chamber can be cleaned. Note the paragraph bridging columns 1 and 2 of this patent. See also column 2, lines 9-14. Note also column 4, lines 39-42, disclosing various cleaning gases which can be used, including, e.g., SF<sub>6</sub>. Note also column 5, lines 25-36, disclosing other cleaning gases which can be used.

Even assuming, arguendo, that the teachings of Benzing were properly combinable with the teachings of Kitsunai, et al., as applied by the Examiner, it is respectfully submitted that such combined teachings would have neither disclosed nor would have suggested the presently claimed method, including wherein the plasma contains, in addition to chlorine gas and hydrobromic gas, Si atoms, as in claim 3, and advantages achieved thereby.

It is emphasized that according to the present invention, the plasma includes Si atoms, the Si atoms participating in the process as described, for example, on pages 13 and 14 of Applicants' specification, noting especially reaction equation (6) on page 14.

In view of the foregoing comments and amendments, reconsideration and allowance of all claims pending in the above-identified application are respectfully requested.

To the extent necessary, Applicants hereby petition for an extension of time under 37 CFR 1.136. Kindly charge any shortage of fees due in connection with the filing of this paper, including any extension of time fees, to the Deposit Account of

Antonelli, Terry, Stout & Kraus, LLP, Account No. 01-2135 (case 648.43608X00),  
and please credit any overpayments to such Deposit Account.

Respectfully submitted,

**ANTONELLI, TERRY, STOUT & KRAUS, LLP**

By /William I. Solomon/  
William I. Solomon  
Registration No. 28,565

WIS/kmh/ksh  
1300 N. 17<sup>th</sup> Street, Suite 1800  
Arlington, Virginia 22209  
Tel: 703-312-6600  
Fax: 703-312-6666